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## Ambient PAH and Metal Concentration in Intertidal Sediments of Coaster's Harbor and Narragansett Bay

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<b>14. ABSTRACT</b>  Previous studies of sediment adjacent to the Old Fire Fighting Training Area (OFFTA) in Coaster's Harbor, Rhode Island, compared values for polynuclear aromatic hydrocarbon (PAH) concentrations for intertidal stations with fully submerged reference stations. NRL and URI have previously reported that the ambient sediment PAH concentrations at that site are low and typical of urbanized estuarine sediments. Bacterial PAH degradation in these sediments results in pool turnover times that suggest the PAH concentrations result from current sources. A Navy fingerprinting study also indicated that the likely source of PAH to Coaster's Harbor sediment is urban runoff. If intertidal and submerged sediments are being impacted by current non-point inputs to surface water, then PAH concentrations may be higher in intertidal sediments. PAHs are relatively hydrophobic and tend to collect at marine interfaces, including the air-sea interface. Wave action in the intertidal zone could deposit hydrophobic contaminants on the surface sediment. An intertidal sediment sampling event was performed in the area adjacent to the OFFTA to evaluate PAH concentrations. In addition, metals analysis was also conducted.								
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# AMBIENT PAH AND METAL CONCENTRATION IN INTERTIDAL SEDIMENTS OF COASTER'S HARBOR AND NARRAGANSETT BAY

## EXECUTIVE SUMMARY

Previous studies of sediment adjacent to the Old Fire Fighting Training Area in Coaster's Harbor, Rhode Island compared values for PAH concentration for intertidal stations with fully submerged reference stations (Battelle Ocean Sciences 1994, Brown and Root 1997, Montgomery et al. 2003). The Naval Research Laboratory and University of Rhode Island (Montgomery et al. 2003) have previously reported that the ambient sediment PAH concentrations at this site are low and typical of urbanized estuarine sediments. In addition, bacterial PAH degradation in these sediments results in contaminant pool turnover times rapid enough to suggest PAH concentrations result from current non-point sources and not historical input (Montgomery et al. 2003). A recent fingerprinting study conducted by the Navy (Emsbo-Mattingly 2002) also indicated that the likely source of PAH to Coaster's Harbor sediment is surface runoff typical of urbanized areas. If intertidal and submerged sediments are being impacted by current non-point inputs to surface water (e.g. street runoff, ship traffic), then PAH concentrations may be higher in intertidal sediments. PAHs are relatively hydrophobic and tend to collect at marine interfaces including the air-sea interface. Wave action in the intertidal zone could deposit hydrophobic contaminants on the surface sediment. An intertidal sediment sampling event was performed from shore by the Naval Research Laboratory and University of Rhode Island on 12 May 2004 in the area adjacent to the Old Fire Fighting Training Area (OFFTA) and various reference areas to evaluate PAH concentrations and spatial distribution within intertidal sediments. In addition, metals analysis was also conducted to assess concentrations and spatial distribution within the same areas.

### PAH Concentration

Total PAH concentrations in nine intertidal sediment samples from Coaster's Harbor and six samples from Narragansett Bay (Figures 1, 2, Table 3) ranged from 0.8 to 24.1 ppm (Table 1). Two of the three highest PAH concentrations (24.1 and 13.5 ppm) were found in the intertidal sediment adjacent to the Middletown boat launch (Latitude: 41°N 34.47000; Longitude: 71°W 17.31040). We previously reported that submerged sediment PAH concentrations near this boat launch reference site were 1.1 ppm (Montgomery et al. 2003). PAH concentrations in the intertidal areas of OFFTA ranged from 1.5 to 21.5 ppm and averaged 7.7 ppm for nine samples whereas the adjacent submerged sediment ranged from 0.11 to 1.3 ppm (Appendix I). PAH concentrations in the six samples from the boat launch and a Tetratech reference area (west side of Narragansett Bay) ranged from 0.8 to 24.1 ppm and averaged 7.1 ppm but the adjacent submerged sediments ranged from 0.03 to 0.22 ppm (Appendix I). For each of these three intertidal sites, the average PAH concentrations from the intertidal sediments are higher than those for the nearby submerged sediment (Montgomery et al. 2003, Appendix I). In addition, the individual PAH compounds that have the highest concentration in the intertidal boat launch sediments (phenanthrene, fluoranthene, and pyrene) are the same compounds that are highest in the most impacted samples from the Coaster's Harbor survey site (Stations 2, 7, 9). These findings support the hypothesis that current surface water inputs are impacting the ambient PAH concentrations in the sediment. Though a major PAH transport study was not performed during the course of this site investigation, the elevated PAH concentrations at the boat launch suggest that local ship traffic may be a significant non-point source. These findings also indicate that submerged reference stations should not be used as reference sites for intertidal sediments because of their differential susceptibility to current day inputs of hydrophobic contaminants to surface waters.

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## Metal Concentration

Metal concentrations (measured by Battelle Marine Sciences Laboratories, Table 2) in Coaster's Harbor sediment were generally unremarkable relative to that reported for natural soil ([http://pubs.usgs.gov/prof/p1634j/html/fm\\_range.htm](http://pubs.usgs.gov/prof/p1634j/html/fm_range.htm)) and compared with the reference sites.

## Conclusions

This sampling compared intertidal sediment reference sites in Narragansett Bay with intertidal sediments from Coaster's Harbor. Previous samplings of intertidal sediment at Coaster's Harbor were compared with submerged sediment at reference sites. Analyses of data collected in previous samplings of the Coaster's Harbor site by Tetrattech (Emsbo-Mattingly 2002), University of Rhode Island (Quinn et al. 1998), Brown and Root Environmental (1997), Battelle Ocean Sciences (1994) and the Naval Research Laboratory (Montgomery et al. 2003) have provided evidence that ambient PAH concentrations are the net result of current day inputs and biodegradation and not the result of historical input. In this study, we found elevated PAH concentrations in the intertidal sediments at both Coaster's Harbor and the boat launch relative to the submerged sediment concentration at both sites. These data support the site conceptual model that non-point source petroleum inputs (e.g. surface runoff, ship traffic) to surface water are the primary influence on ambient PAH concentrations in Coaster's Harbor sediments. Petroleum input via this pathway to these intertidal sediments would be exposed to rapid photodegradation, volatilization, and biodegradation in this relatively high energy environment. The alternate site conceptual model that the PAH concentrations in the submerged and intertidal sediments are the result of historical input is not supported by the data. In the absence of substantial, conflicting information on PAH flux and transport in Coaster's Harbor, it is not scientifically defensible to expect that removal or manipulation of either the submerged or intertidal sediments will result in a net long term reduction in ambient PAH concentrations. In addition, it is recommended that in the future any intertidal sediment samples collected in Coaster's Harbor, adjacent to the OFFTA site, be compared to reference samples that are also collected from intertidal areas with similar environmental influences.

Figure 1. Sample locations for stations 1-9 at OFFTA in Coaster's Harbor for May 2004.

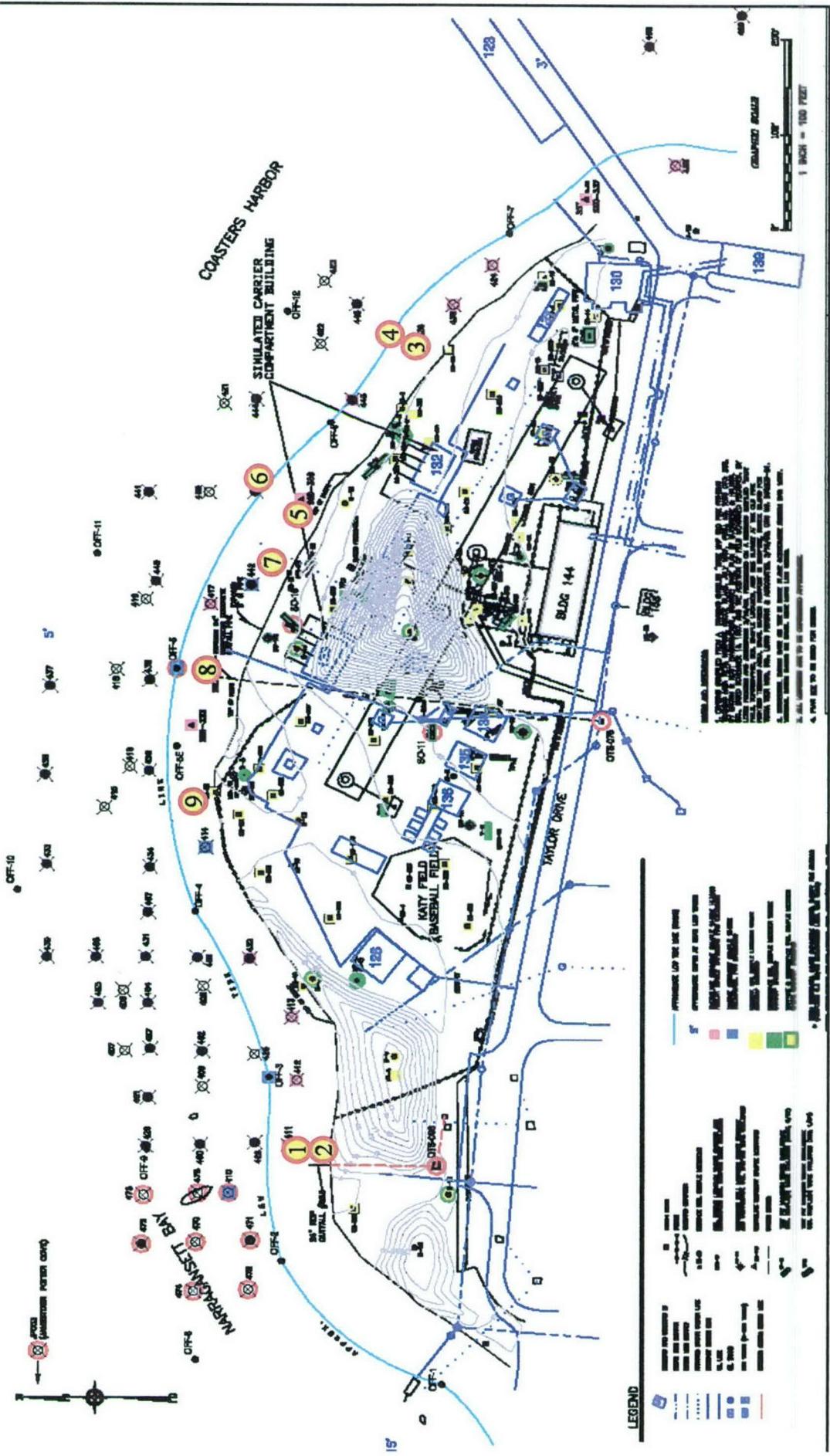


Figure 2. May 2004 sampling stations for Middleton boat launch (Stations 10M (high), 11M (mid), 12M (low water line)) and for the Tetratech background site on the west side of Narragansett Bay (Stations 13B (high), 14B (mid), 15B (low water line)).

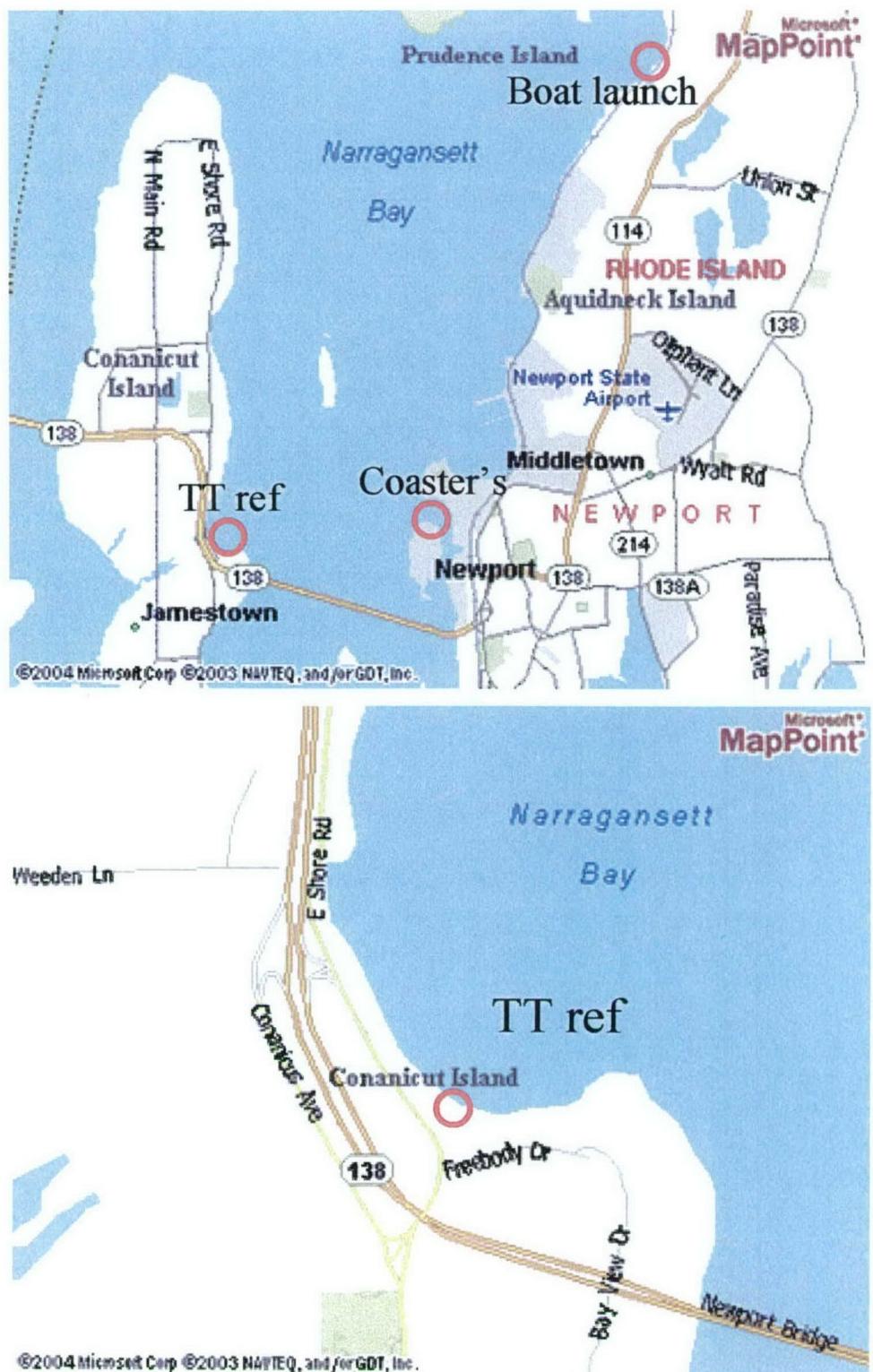


Table 1. Individual and total PAH concentrations (ppm) for intertidal sediment in Coaster's Harbor (Stations 1-9), the Middleton boat launch (Stations 10M-12M), and the west Bay reference site (Stations 13V-15B) for May 2004.

	Total																
	Benzo[g,h,i]perylene	Dibenz[a,h]anthracene	Indeno[1,2,3-cd]pyrene	Benzo[a]pyrene	Benzo[k]fluoranthene	Benzo[b]fluoranthene	Chrysene	Benzof[a]anthracene	Pyrene	Fluoranthene	Anthracene	Phenanthrene	Fluorene	Biphenyl	Acenaphthylene	Naphthalene	Station
<b>1</b>	0.01	0.03	0.00	0.01	0.17	0.04	0.33	0.12	0.12	0.08	0.09	0.09	0.00	0.06	0.06	1.5	
<b>2</b>	0.17	0.95	0.08	0.30	4.61	0.77	5.52	4.51	0.45	0.78	0.72	0.80	0.89	0.11	0.42	0.39	21.5
<b>3</b>	0.02	0.09	0.01	0.04	0.56	0.12	0.75	0.64	0.22	0.19	0.10	0.12	0.12	0.02	0.07	0.07	3.1
<b>4</b>	0.04	0.08	0.01	0.02	0.42	0.10	0.57	0.49	0.13	0.13	0.06	0.07	0.07	0.01	0.04	0.05	2.3
<b>5</b>	0.04	0.23	0.01	0.06	0.98	0.23	1.38	1.05	0.33	0.27	0.13	0.16	0.17	0.01	0.10	0.09	5.2
<b>6</b>	0.12	0.37	0.03	0.11	1.76	0.20	2.43	2.13	0.61	0.48	0.33	0.39	0.43	0.06	0.25	0.25	9.9
<b>7</b>	0.09	0.42	0.02	0.10	2.14	0.44	2.64	1.97	0.59	0.47	0.22	0.26	0.29	0.04	0.16	0.14	10.0
<b>8</b>	0.07	0.30	0.03	0.14	2.84	0.62	2.46	1.91	0.61	0.49	0.24	0.29	0.30	0.04	0.16	0.14	10.6
<b>9</b>	0.06	0.26	0.02	0.14	2.08	0.36	0.12	1.01	0.28	0.23	0.11	0.13	0.14	0.02	0.08	0.06	5.1
<b>10M</b>	0.08	0.00	0.34	0.27	2.64	0.56	2.42	2.39	0.99	0.97	0.56	0.56	0.81	0.11	0.35	0.42	13.5
<b>11M</b>	0.11	0.00	0.71	0.62	5.49	1.20	5.22	4.24	0.47	1.22	1.09	1.18	1.42	0.15	0.27	0.74	24.1
<b>12M</b>	0.01	0.00	0.03	0.03	0.30	0.05	0.34	0.37	0.18	0.21	0.10	0.10	0.16	0.02	0.08	0.09	2.1
<b>13B</b>	0.00	0.07	0.00	0.00	0.07	0.03	0.20	0.20	0.08	0.09	0.05	0.05	0.06	0.01	0.03	0.03	1.0
<b>14B</b>	0.00	0.05	0.01	0.00	0.05	0.03	0.18	0.18	0.07	0.07	0.04	0.04	0.05	0.00	0.03	0.03	0.8
<b>15B</b>	0.00	0.09	0.02	0.01	0.06	0.00	0.17	0.19	0.07	0.07	0.04	0.04	0.05	0.01	0.03	0.03	0.9

Table 2. Metals concentrations (ppm) for intertidal sediment in Coaster's Harbor (Stations 1-9), the Middleton boat launch (Stations 10M-12M), and the west Bay reference site (Stations 13V-15B) for May 2004.

BATTELLE MARINE SCIENCES LABORATORIES									
SPONSOR CODE	Percent Moisture	Ag	Al	As	Ba	Be	Ca	Cd	
			ICP- OES	ICP-MS	ICP- OES	ICP- OES	ICP- OES	ICP- OES	ICP-MS
	Method:	GFAA							
	Digestion:	BA	BA	SE	BA	BA	BA	BA	SE
<b>Achieved MDLs<sup>1</sup></b>		<b>0.0280</b>	<b>7.17</b>	<b>0.0277</b>	<b>0.104</b>	<b>0.0262</b>	<b>1.24</b>	<b>0.0105</b>	
<b>Achieved RLs<sup>2</sup></b>		<b>0.0890</b>	<b>22.8</b>	<b>0.088</b>	<b>0.331</b>	<b>0.0833</b>	<b>3.94</b>	<b>0.0334</b>	
NRL-1	10.2	0.0334	J	40030	5.01	278	1.35	29655	0.203
NRL-2	6.01	0.0327	J	50467	5.21	488	1.99	6872	0.331
NRL-3	7.39	0.0280	U	44128	5.87	325	1.54	57156	0.196
NRL-4	26.2	0.140		41634	4.24	399	1.44	11124	0.283
NRL-5	17.7	0.0404	J	41262	6.60	344	1.29	22158	0.296
NRL-6	25.3	0.0531	J	36540	5.93	335	1.17	26051	0.314
NRL-6	25.3	0.0524	J	40242	4.15	675	1.28	18775	0.285
NRL-7	8.03	0.0677	J	45834	7.91	386	1.51	31217	0.265
NRL-8	10.7	0.0488	J	42254	6.06	337	1.49	24187	0.214
NRL-9	4.18	0.0280	U	46505	15.0	295	1.67	20207	0.204
NRL-10M	3.26	0.0280	U	32911	5.75	275	1.06	5492	0.174
NRL-11M	11.3	0.0280	U	33440	2.84	306	1.05	4997	0.115
NRL-12M	3.55	0.0280	U	33611	4.49	270	1.12	13401	0.131
NRL-13B	18.4	0.0280	U	38723	1.44	335	1.33	4722	0.174
NRL-14B	16.0	0.0280	U	42271	1.63	330	1.53	5765	0.189
NRL-15B	16.9	0.0280	U	36212	1.68	312	1.34	5112	0.242

Table 2. Metals concentrations (ppm; continued).

BATTELLE MARINE SCIENCES LABORATORIES								
SPONSOR CODE	Percent Moisture	Co	Cr	Cu	Fe	Hg	K	Mg
Method:	ICP-MS	ICP-MS		ICP- MS	ICP- OES	CVAA	ICP- OES	ICP- OES
Digestion:	SE	SE		SE	BA	SE	BA	BA
<b>Achieved MDLs<sup>1</sup></b>	<b>0.0103</b>	<b>0.0631</b>		<b>0.153</b>	<b>1.0</b>	<b>0.0043</b>	<b>1.05</b>	<b>1.29</b>
<b>Achieved RLs<sup>2</sup></b>	<b>0.0328</b>	<b>0.201</b>		<b>0.487</b>	<b>3.2</b>	<b>0.014</b>	<b>3.34</b>	<b>4.10</b>
NRL-1	10.2	7.47		29.1	16.8	20129		12643
NRL-2	6.01	7.28		25.7	19.1	29820		18035
NRL-3	7.39	7.85		22.8	12.5	23434		14698
NRL-4	26.2	6.12		23.5	20.1	21520		16820
NRL-5	17.7	8.11		35.5	19.3	26629		15044
NRL-6	25.3	7.18		31.1	28.9	25071		14764
NRL-6	25.3	5.42		27.6	20.6	51364		14289
NRL-7	8.03	10.2		36.5	22.0	28664		17895
NRL-8	10.7	7.03		34.6	18.4	31443		16100
NRL-9	4.18	14.3		33.7	31.9	27233		16466
NRL-10M	3.26	8.00		19.1	13.2	25203		10156
NRL-11M	11.3	3.65		19.2	8.60	13050		12773
NRL-12M	3.55	4.60		21.2	13.9	15238		11447
NRL-13B	18.4	4.88		24.8	10.8	15362		15055
NRL-14B	16.0	6.57		24.2	9.90	22802		16259
NRL-15B	16.9	5.22		23.1	10.7	17618		3174

Table 2. Metals concentrations (ppm; continued).

BATTELLE MARINE SCIENCES LABORATORIES								
SPONSOR CODE	Percent Moisture	Ni	Pb	Sb	Se	Tl	V	Zn
	Method:	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
	Digestion:	SE	SE	SE	SE	SE	SE	SE
<b>Achieved MDLs<sup>1</sup></b>	<b>0.0538</b>	<b>0.0429</b>	<b>0.00330</b>	<b>0.181</b>	<b>0.0115</b>	<b>0.111</b>	<b>0.459</b>	
<b>Achieved RLs<sup>2</sup></b>	<b>0.171</b>	<b>0.136</b>	<b>0.0105</b>	<b>0.576</b>	<b>0.0366</b>	<b>0.353</b>	<b>1.46</b>	
<hr/>								
NRL-1	10.2	14.9	52.8	0.697	0.181	U	0.358	46.2
NRL-2	6.01	17.0	52.5	0.738	0.181	U	0.396	46.4
NRL-3	7.39	18.8	26.3	0.359	0.181	U	0.183	45.5
NRL-4	26.2	12.2	46.8	0.698	0.181	U	0.358	48.5
NRL-5	17.7	17.7	43.3	0.709	0.181	U	0.455	66.5
NRL-6	25.3	17.4	53.1	0.765	0.181	U	0.349	128
NRL-6	25.3	13.0	65.3	0.912	0.181	U	0.357	138
NRL-7	8.03	21.2	54.2	0.705	0.181	U	0.435	45.6
NRL-8	10.7	16.6	70.2	0.952	0.181	U	0.354	102
NRL-9	4.18	22.9	50.9	0.991	0.181	U	0.291	61.3
NRL-10M	3.26	20.6	12.0	0.307	0.181	U	0.286	66.3
NRL-11M	11.3	8.36	13.1	0.243	0.181	U	0.289	32.1
NRL-12M	3.55	11.4	12.5	0.335	0.181	U	0.331	54.2
NRL-13B	18.4	11.2	13.3	0.189	0.181	U	0.366	36.0
NRL-14B	16.0	11.2	12.7	0.131	0.181	U	0.372	36.7
NRL-15B	16.9	9.61	14.1	0.178	0.181	U	0.345	61.0
								63.2

Table 3. Sample locations for OFFTA stations in Northings and Eastings, or latitude and longitude for reference stations for May 2004.

Station		Coordinates	
NRL	Site	Northing	Easting
1	OFFTA	157003	546800
2		156988	546803
3		156875	547695
4		156890	547706
5		157035	547465
6		157072	547480
7		157098	547395
8		157098	547280
9		157115	547200
		Latitude (41°N)	Longitude (71°W)
10M	Boat Launch	34.4700	17.31040
11M		34.4700	17.31040
12M		34.4700	17.31040
13B	TetraTech Bay Reference	30.6470	21.7300
14B		30.6470	21.7300
15B		30.6470	21.7300

## **Supporting References**

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## Appendix I

### Data from the second NRL sampling (October 2002) of OFFTA in Coaster's Harbor and reference stations in Narragansett Bay.

Figure A1. Sample locations for stations 1-8 at Coaster's Harbor for October 2002.

Figure A2. Sampling stations for submerged sediment from the Tetratex background site on the west side of Narragansett Bay (Stations 9), off the McAllister Point landfill (Station 10) and off the Middleton boat launch (Station 11) for October 2002.

Table A1. PAH concentrations in Coaster's Harbor and Narragansett Bay sediment ranged from 0.08 to 1.33 ppm during October 2002 sampling. Ambient PAH concentration was low (< 12 ppm) for three samplings in '02 compared to 6-132 ppm in (Battelle Ocean Sciences 1994), 47 ppm in '97 (Brown and Root Environmental 1997), and to >4 ppm (7 stations), >44 ppm (4 stations) and >132 ppm (1 station) in '98 (Quinn et al. 1998).

Table A2. Mineralization rates for naphthalene, phenanthrene and fluoranthene in Coaster's Harbor and Narragansett Bay sediment for October 2002 sampling. PAH mineralization rates were consistent with those found in other estuarine sediment sites with low PAH concentration and flux.

Table A3. Turnover times for PAHs in Coaster's Harbor and Narragansett Bay sediment for October 2002 sampling. PAH turnover was rapid enough to metabolize current PAH flux through sediment in days to months to two years. This is consistent with the attenuation of ambient PAH concentration at the site since 1994.

Table A4. Bacterial production in sediments of Coaster's Harbor and Narragansett Bay sediment for October 2002 sampling was within the range typically found for sediments in urbanized estuaries.

Figure A1. Sample locations for stations 1-8 at Coaster's Harbor for October 2002.

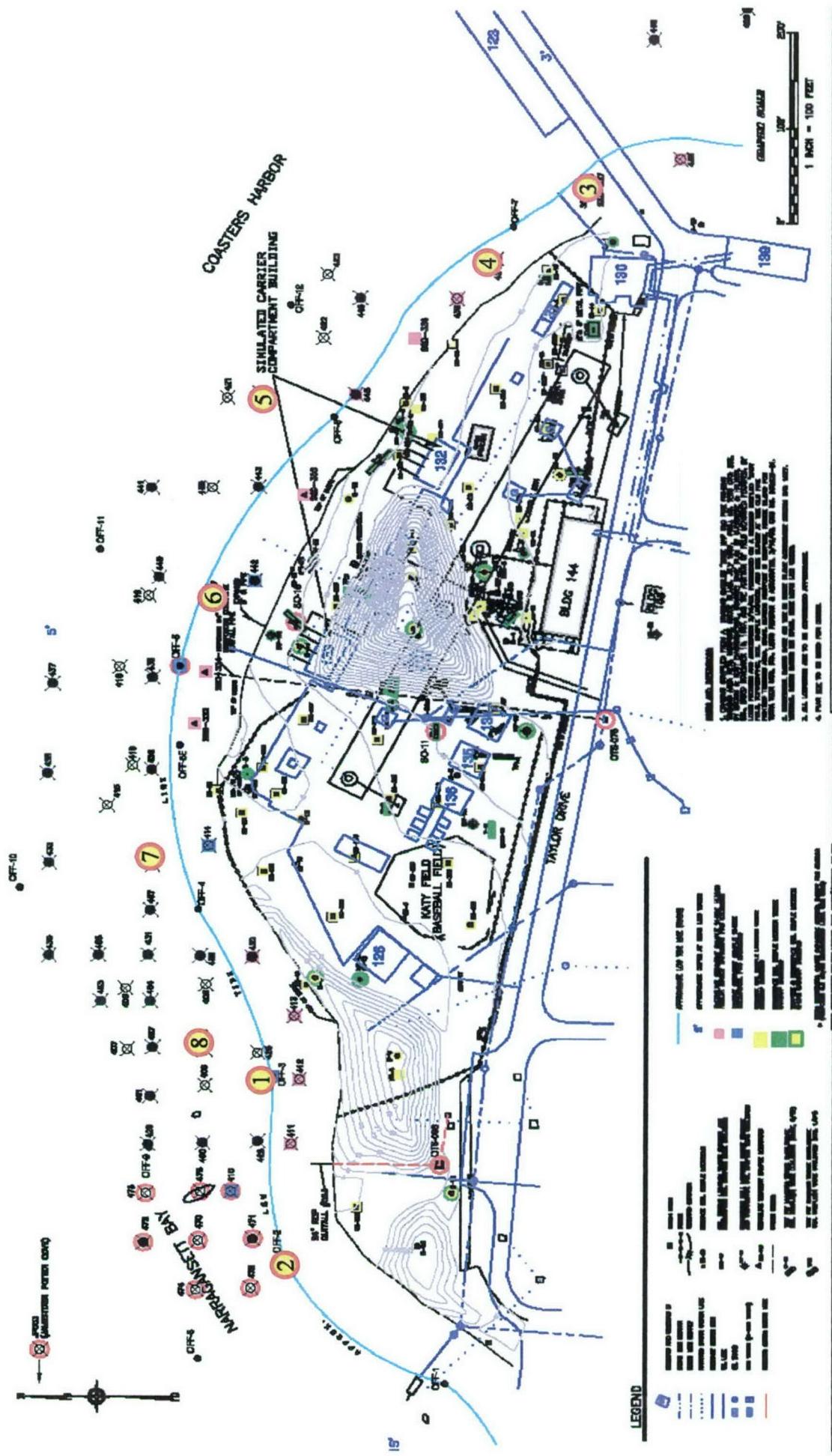


Figure A2. Sampling stations for submerged sediment from the Tetrach background site on the west side of Narragansett Bay (Stations 9), off the McAllister Point landfill (Station 10) and off the Middleton boat launch (Station 11) for October 2002.

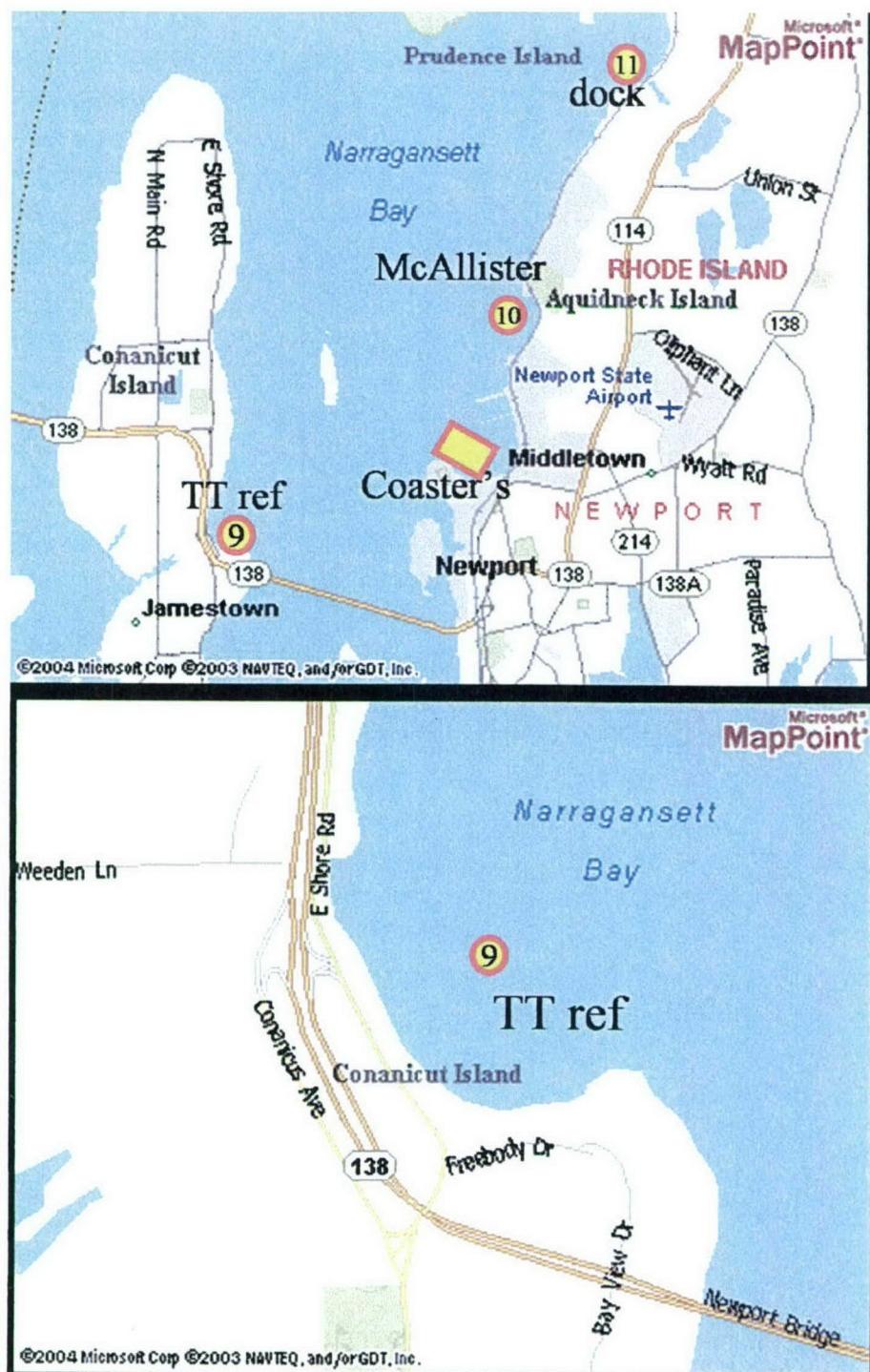


Table A1. PAH concentrations in Coaster's Harbor and Narragansett Bay sediment ranged from 0.08 to 1.33 ppm during October 2002 sampling. Ambient PAH concentration was low (< 12 ppm) for three samplings in '02 compared to 6-132 ppm in (Battelle Ocean Sciences 1994), 47 ppm in '97 (Brown and Root Environmental 1997), and to >4 ppm (7 stations), >44 ppm (4 stations) and >132 ppm (1 station) in '98 (Quinn et al. 1998).

Tetratech	NRL	Total PAH (ppm)
OFF-3	1	0.96
OFF-2	2	0.24
SSD-337	3	0.98
424	4	1.33
444	5	0.41
417	6	0.15
434	7	0.08
462	8	0.11
Reference	9	0.03
MacAllister	10	0.08
dock	11	0.22

Table A2. Mineralization rates for naphthalene, phenanthrene and fluoranthene in Coaster's Harbor and Narragansett Bay sediment for October 2002 sampling. PAH mineralization rates were consistent with those found in other estuarine sediment sites with low PAH concentration and flux.

Station	Mineralization Rate ( $\mu\text{g g}^{-1} \text{d}^{-1}$ )					
	Naphthalene		Phenanthrene		Fluoranthene	
	AVG	SD	AVG	SD	AVG	SD
1	1.09E-05	7.76E-05			2.11E-04	7.26E-04
2			3.50E-03	7.98E-03	1.94E-05	3.36E-05
3	4.67E-04	2.41E-04	2.91E-03	3.24E-03		
4	1.79E-05	6.11E-05				
6	9.67E-04	2.35E-04	3.98E-03	2.55E-03	1.89E-03	2.13E-03
7			5.09E-04	1.11E-02		
8	8.52E-05	1.29E-04				
9	1.38E-04	4.36E-05				
10	3.26E-04	2.20E-04	3.75E-03	1.02E-03		

Table A3. Turnover times for PAHs in Coaster's Harbor and Narragansett Bay sediment for October 2002 sampling. PAH turnover was rapid enough to metabolize current PAH flux through sediment in days to months to two years. This is consistent with the attenuation of ambient PAH concentration at the site since 1994.

Station	PAH Turnover Time (days)	
	Phenanthrene	Fluoranthene
1		939
2	11	3257
3	62	
4		
6	9	18
7	18	
8		
9		
10	4	

Table A4. Bacterial production in sediments of Coaster's Harbor and Narragansett Bay sediment for October 2002 sampling was within the range typically found for sediments in urbanized estuaries.

Station	Sample Type	Bacterial Production ( $\mu\text{g C kg}^{-1} \text{ d}^{-1}$ )	
		AVG	SD
1	sediment	7.9	2.3
2	sediment	6.7	1.0
3	sediment	20.3	7.5
4	sediment	10.0	3.9
5	sediment	8.7	1.3
6	sediment	11.8	0.9
7	sediment	5.8	1.7
8	sediment	9.7	5.4
9	sediment	9.9	1.5
10	sediment	4.5	0.0
11	sediment	12.4	1.9

## **Appendix II**

### **Pictures of intertidal locations from May 2004 sampling event.**

Figure B1. May 2004 sampling locations at OFFTA for NRL-1, NRL-5, and NRL-8.

Figure B2. May 2004 sampling locations at the Middleton Marina for NRL-10M and NRL-11M.

Figure B3. May 2004 sampling locations near the TetraTech west Narragansett Bay reference site for NRL-14B and NRL-15 M.

Figure B1. May 2004 sampling locations at OFFTA for NRL-1, NRL-5, and NRL-8.



Figure B2. May 2004 sampling locations at the Middleton Marina for NRL-10M and NRL-11M.



Figure B3. May 2004 sampling locations near the TetraTech west Narragansett Bay reference site for NRL-14B and NRL-15M.

